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ARF 1184-8

(Quarterly Report No. 8)

MAGNETIC PROPERTIES OF INSULATORS

to

US Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

ARMOUR RESEARCH FOUNDATION
of
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

ARF 1184-8
(Quarterly Report No. 8)

on

MAGNETIC PROPERTIES OF INSULATORS
Contract No. At(11-1)-578
Project Agreement No. 9

to

US Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

Attention: Fred C. Mattmueller
Acting Director
Contract Division

(Covering the period from November 16, 1962 to February 15, 1963)

March 1, 1963

FORWARD

This quarterly progress report summarizes three activities of the group within the last three months.

A careful study of the ratio of the maximum absorption of the K band to the maximum absorption of the F band has been made in additively colored and γ -irradiated RbCl. The range in imperfection concentration is such that the absorption in the F region of the spectrum can be measured carefully. The variation is much larger than in KCl colored by X-rays. Our tentative conclusion is that the F and K bands do not come from the same imperfection. At present our understanding of the excited state of the F center is extremely limited. It is our hope that further detailed studies will resolve some of these problems. This work was done by Mr. George Stungis and Dr. G. A. Noble with the guidance of the principal investigator.

We have been fortunate to have Dr. Y. Brada from Hebrew University Jerusalem, Israel join our group for about two years. He plans to extend the luminescence work of Lütty and Gebhardt to RbCl. The ability to resolve the K band in this alkali halide makes it attractive for this work. On the other hand purified crystals are needed to make the results more reliable. We believe we have obtained purer crystals from the Anderson Laboratories in Urbana, Illinois. Dr. Brada will have the primary responsibility of the optical work although Dr. Noble will continue to be responsible for the overall experimental aspects of the problem.

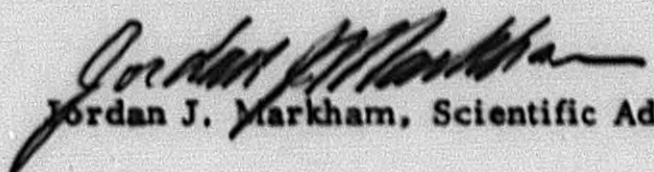
We have been continuing our theoretical study of the lifetime of the excited state of the F center in KCl. We now understand the reasons for the sizeable difference in the lifetime calculation of Fowler and Dexter and those

of the author. At present no satisfactory explanation of the difference between the theoretical values and the experimental values of Swank and Brown exist, however.

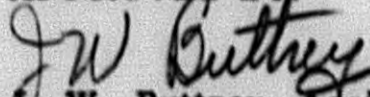
Dr. Noble is starting to build a new spectrometer for EPR work and Mr. Casselman continues his calculations of spin-lattice relaxation times.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION
of Illinois Institute of Technology


Jordan J. Markham, Scientific Advisor

APPROVED BY:


J. W. Buttrey, Assistant Director
of Physics Research

I. THE RATIO OF THE K-BAND TO THE F-BAND IN RbCl

A. HISTORICAL INTRODUCTION

In the early experiments of Kleinschrod¹ on additively colored KCl, a small absorption band known as the K-band was found on the violet side of the F-band. The optical absorption measurements were performed at room temperature, where there is a poor resolution between the K and F bands. Later, measurements by Pick² on additively colored crystals at 38°K showed an absence of the K-band. Both Kleinschrod and Pick used identical methods of sample preparation. A difference did exist, however; Pick heated and quenched his samples before measurement while Kleinschrod did not. Since the absorption was measured at a limited number of points, Pick may have just missed the small K-band.

Theoretically the absorption spectra of a trapped electron should consist of a series of lines which broaden because of the electron lattice interactions. A series limit should exist beyond which a continuous absorption band lies. Mott and Gurney³ suggested that since the F-center absorption was due to a $1s \rightarrow 2p$ type transition of the trapped electron, the K-band could be attributed to a $1s \rightarrow np$ type transition. If the K-band is due to a higher excited state of the F-center, the ratio of their maximum absorption coefficients should be constant (provided that there are no extraneous perturbations present, such as two interacting F-centers which could depend on the F-center concentration).

Geiger and Etzel⁴ studied the K-band in additively colored KCl. They bleached the F-band at 50° C for small periods of time. Their data indicates not only the expected growth of M and R bands but also an unexpected growth in the K-band. The calculated ratio of K/F then showed a significant vari-

ation, from which they concluded that the K-band was not due to a transition of an electron in the ground state of the F-center to excited states or to the conduction band.

Later Geiger⁵ independently measured the ratio of the K and F-band absorption coefficients in additively colored KCl. The crystals were colored and quenched with no subsequent bleaching, heating or quenching performed on them. He found a variation in the K to F ratio of approximately seven-teen percent. However, in the data that was presented there existed a sizeable absorption due to M and R centers. The presence of the other centers tends to distort the F-band, possibly giving rise to the observed variation in the ratio.

Markham and Duerig measured the ratio in KCl and found a value of 0.047 at 78°K, which was communicated to Prof. Seitz.⁶ Konitzer and Markham⁷ studied the effects of bleaching the F-band. Their data also indicated a variation in the K to F ratio because of bleaching. It is interesting to note that the K to F ratio in additively colored unbleached KCl samples exhibited as much as a fifty percent variation. The ratio change from 4.8 to 3.2 which could be real or could be due to changes in the base line. This is one of the difficulties of knowing for sure if the ratio really varies (see Konitzer and Markham^{7a})

Lüty⁸ examined the properties of the K-band in many of alkali halides. His measurements were performed at 93°K. The concentration of F-centers were varied from 2×10^{16} to 2×10^{18} in KCl and 6×10^{16} to 7×10^{17} in RbCl. He found that the K to F ratio was .046 in KCl and .0545 in RbCl. His measurements indicated the following: - (1) The K/F ratio is independent of concentration in all alkali halides. (2) The K to F ratio is different in

different alkali halides and seems to be greatest in the bromides. (3) The shape of the K-band is temperature independent and its half-width is equal to the half-width of the F-center at room temperature. From the above experimental consideration, Lütj then concluded that the K-band represents a transition to higher excited states of the F-center electron. Lütj believes that the previously reported variation was due to a band or series of bands which formed under the F and K. This occurred, he believed, when the F-band was bleached optically. This was an extremely reasonable point of view.

Brown and Wild⁹ measured the photo-conductivity properties at 10°K and 78°K on the high energy side of the F-band in additively colored KCl. They found that the product of the quantum yield and carrier range at 10°K was independent of wavelength in the region of the L-bands reported by Lütj;⁸ however, they found that it decreases rapidly with increasing wavelength in the region of the K and F band. At 10°K, they found the value of the quantum yield was 2.7×10^{-4} for the F-band and 4.6×10^{-3} for the K-band. The sudden decrease in quantum yield in the region of the K and F bands agrees with the suggestion that the K band results from excitation to states below the conduction band.

One must be skeptical in accepting the work of Brown and Wild and of Lütj as conclusively showing that the K-band is a bound state transition to a higher excited state of the F-center. First, the change in the K to F ratio when the F-center is bleached is not completely explained by Lütj. A second problem is the high concentration at which Lütj's experiments were performed. At the high concentrations used, it is extremely difficult to obtain "pure" F-centers and, therefore, it probably is not correct to speak of

a K to F ratio. A third difficulty is the temperature independence of the width of the K-band found by Lüty. If the K-band arises from a bound transition, one would expect a temperature dependence of width. (See for example Ref. 10). Even at low temperatures, however, there is a high degree of overlap between the K and F bands. This makes the determination of the shape and the width very difficult.

B. STUDY OF THE K TO F RATIO IN RbCl

The purpose of this experimental study is to determine whether the K to F ratio is a constant. In order to do this we will restrict ourselves to pure F-centers.¹¹ We assume that the band with small H values, defined below, is associated with "pure" F-centers. There is evidence from optical and EPR work that this is indeed the case; the evidence, however, is not conclusive. If, however, other bands do appear, we will try to correlate them with a variation in the ratio.

The questions that we seek to answer are the following:

- (1) If the range of concentration is restricted such that one obtains good optical measurements does the K to F ratio depend on the F-center concentration?
- (2) If we characterize the pure F-center by the parameter ϵ_v , ϵ_r , and $H = (\epsilon_v - \epsilon_r)$ do small concentrations of the other centers (i. e., such as M, R, N and K_1 ¹¹ centers) affect these values and also the K to F ratio.

Sample Preparation

Samples of RbCl obtained from Semi-Elements and those obtained from Korth were colored by means of γ -irradiation and additive coloration.

TABLE I - K to F Ratio in X-irradiated KCl
Measurements are at 78°K.

<u>No.</u>	<u>$\alpha_m(K)/\alpha_m(F)$</u>
1.	0.044
2.	0.049
3.	0.048
4.	0.050
5.	0.045
6.	0.048
7.	0.048
8.	0.047
9.	0.049

(Data taken at the Applied Physics Laboratory Johns Hopkins
University)

TABLE II
 SUMMARY OF DATA
 K to F ratio in Additively Colored KCl

Measurements made at 78°K

<u>H(ev)</u>	<u>$\alpha_m(M)/\alpha_m(F)$</u>	<u>$\alpha_m(K)/\alpha_m(F)$</u>
.193	0.012	0.040
.195	0.017	0.032
.195	0.070	0.038
.196	0.014	0.036
.196	0.016	0.041
.196	0.058	0.048
.197	0.011	0.038

TABLE III - Summary of K to F Ratio Measurements in
 δ -irradiated and additively colored RbCl at 78°K

No.	ϵ_v (ev)	ϵ_r (ev)	H (ev)	$\frac{\alpha_m(K)}{\alpha_m(F)}$	$\frac{\alpha_m(M)}{\alpha_m(F)}$	$\frac{\alpha_m(K_1)}{\alpha_m(F)}$	N_f
1	2.137	1.952	.185	.058	.045	.035	6.95×10^{16}
2	2.137	1.958	.179	.057	.095	.053	5.64×10^{16}
3	2.144	1.958	.186	.096	.101	.040	8.64×10^{16}
4	2.148	1.952	.196	.052	.045	.186	6.1×10^{15}
5	2.148	1.958	.190	.044	0	.165	6.1×10^{15}
6	2.148	1.958	.190	.058	.094	.043	4.7×10^{16}
7	2.148	1.958	.190	.049	.012	0	3.72×10^{16}
8	2.148	1.958	.190	.052	.017	0	7.4×10^{16}
9	2.156	1.964	.192	.049	.014	0	4.23×10^{16}
10	2.148	1.958	.190	.060	.027	0	3.68×10^{16}
11	2.163	1.946	.217	.057	.010	0	1.0×10^{16}
12	2.152	1.958	.196	.070	.020	.203	6.86×10^{15}
13	2.137	1.974	.170	.039	.020	.032	1.16×10^{16}
14	2.137	1.967	.170	.038	.010	.085	6.2×10^{15}
15	2.144	1.940	.204	.060	.060	.300	6.65×10^{15}
16	2.150	1.940	.210	.092	0	.258	5.24×10^{15}
17	2.142	1.952	.190	.032	0	.053	3.31×10^{15}
18	2.142	1.951	.191	.045	.005	.045	4.33×10^{15}
19	2.142	1.952	.190	.044	.020	.117	5.1×10^{15}
20	2.142	1.952	.190	.063	0	.054	6×10^{15}

α_m (K) maximum absorption of the K band

We do not believe these crystals were exceptionally pure. The technique involved in coloration has been previously described.¹¹ The range of F-center concentration was chosen so that good optical measurements could be made. (i. e., from $10^{15} \frac{\text{centers}}{\text{cm}^3}$ to $10^{17} \frac{\text{centers}}{\text{cm}^3}$).

The samples were mounted in a modified Hersh type Dewar and optical absorption measurements were made at 78°K with a Cary 14 Spectrophotometer.

Discussion of Results

Table III illustrates the range of concentration and subsequent values obtained from measurements of the optical absorption spectra. Since the K, K₁, and M bands are small the baseline is very important. Some of the variations are due to changes in the base line but we believe that the variation is too large to explain in this manner. A typical set of data illustrating the K to F ratio in KCl is shown in Tables I and II. Table I shows an extremely small deviation in the K to F ratio for x-irradiated KCl at liquid nitrogen temperatures. Table II indicates a rather large variation in additively colored KCl at liquid nitrogen temperatures. It is interesting to note, however, that one cannot correlate this variation with any subsequent variation in the M to F ratio or the F-band half-width, H. Hence, we strongly believe we are reporting genuine changes in the K to F ratio. There seems to exist a large variation in the K to F ratio. The variation in ϵ_v , ϵ_r and H from sample to sample is much larger than in KCl. We do not understand the reason for this at present.

Figure 1 compares the absorption spectra of two samples of additively colored RbCl. The band appearing at 2.4 ev is the K-band. Here

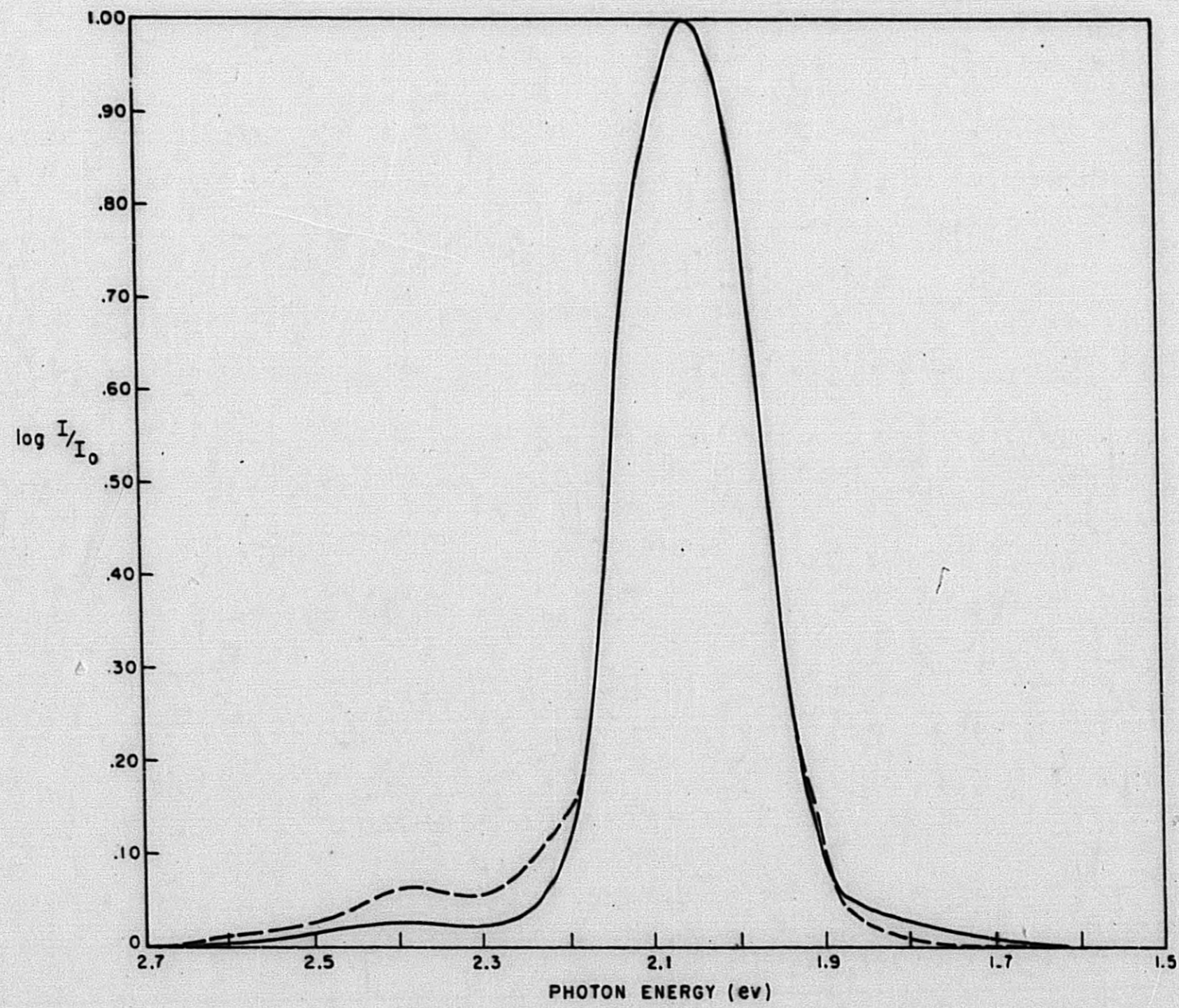


Figure I Comparison of the Normalized optical absorption spectra of the F-center in RbCl for two samples at concentrations of 3×10^{16} (dashed curve) and 6×10^{15} (solid curve).

a large difference in the K to F ratio is shown. There is a slight difference in the tails on the red side of the F-band. This variation could be due to the formation of a K_1 -band.

In order to ascertain whether the change in the K to F ratio is due to structure appearing on the red side, Figures 2 and 3 were constructed. Figure 2 is a graph of the K to F ratio versus the M to F ratio at 78°K . It is interesting to note that one obtains a large spread in the values of the K to F ratio when the M-center concentration is approximately zero. Also the deviations seem to be independent of the method of coloration.

Figure 3 is a graph of the K to F ratio versus the K_1 to F ratio at 78°K . Here again we immediately note a large deviation in the K to F ratio when the K_1 -band does not appear. When the value of K_1 to F is exceedingly large, there does not seem to be a large deviation in the K to F ratio. Thus, we can conclude that the K-band is independent of the K_1 -band.

Figure 4 is a graph of the K to F ratio versus the F-center concentration N_f . The concentration range as mentioned before, was chosen so that good optical measurements could be made. There does not seem to be an obvious relation between the K to F ratio and N_f .

In order to ascertain whether or not we have pure F-centers present, Figure 5 was constructed. Here we have a graph of the K to F ratio versus the parameters characterizing the F-band, ϵ_v and ϵ_r . We note that the presence of the K_1 -band does not alter the violet side of the F-band. It does seem to have some affect on ϵ_r ; however, the deviations are quite small and are assumed to be due to errors in determining the baseline on the red side.

Figure 6 is a graph of the K to F ratio versus the parameters ϵ_v and

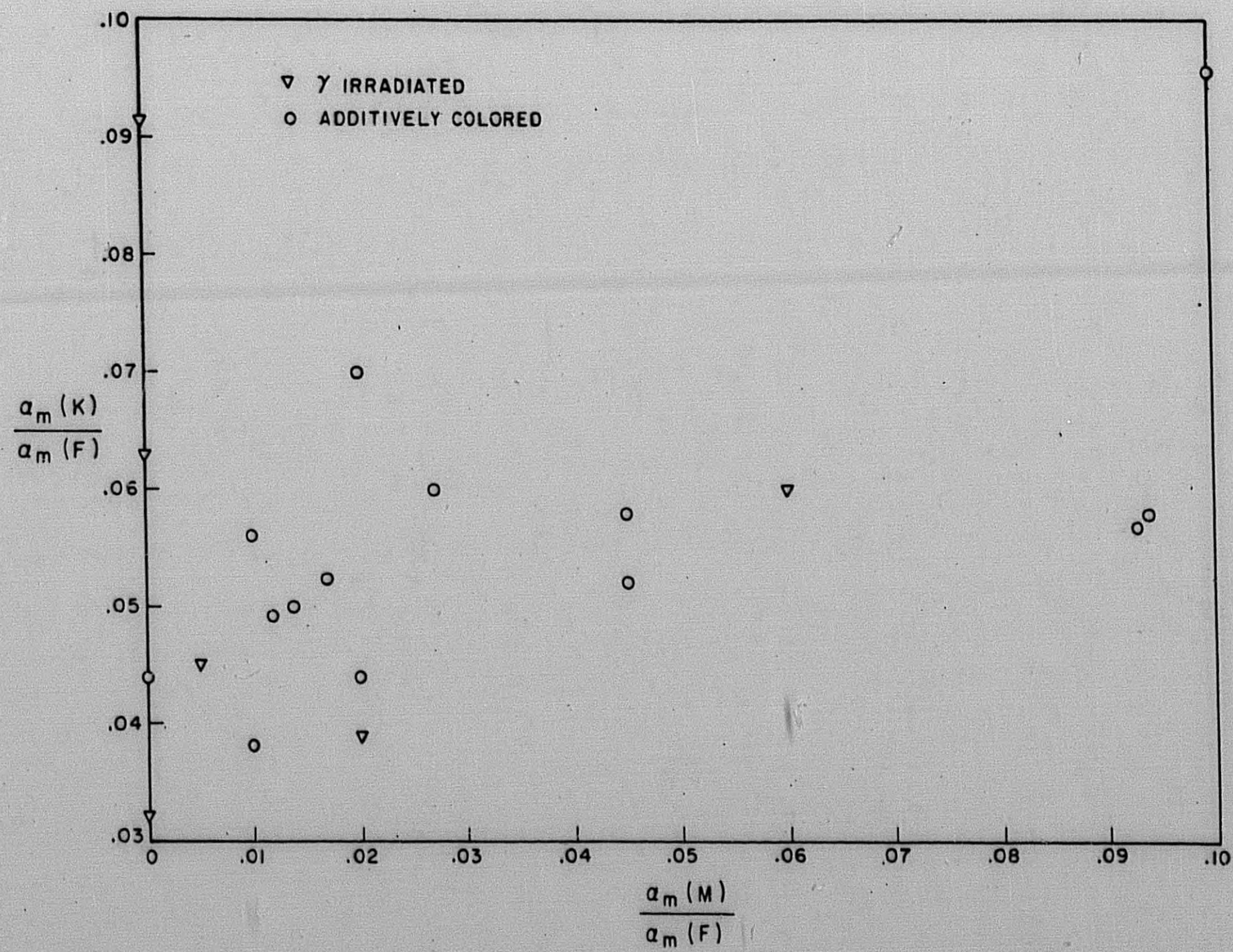


Figure 2. The K to F ratio versus the M to F ratio for γ -irradiated and additively colored RbCl.

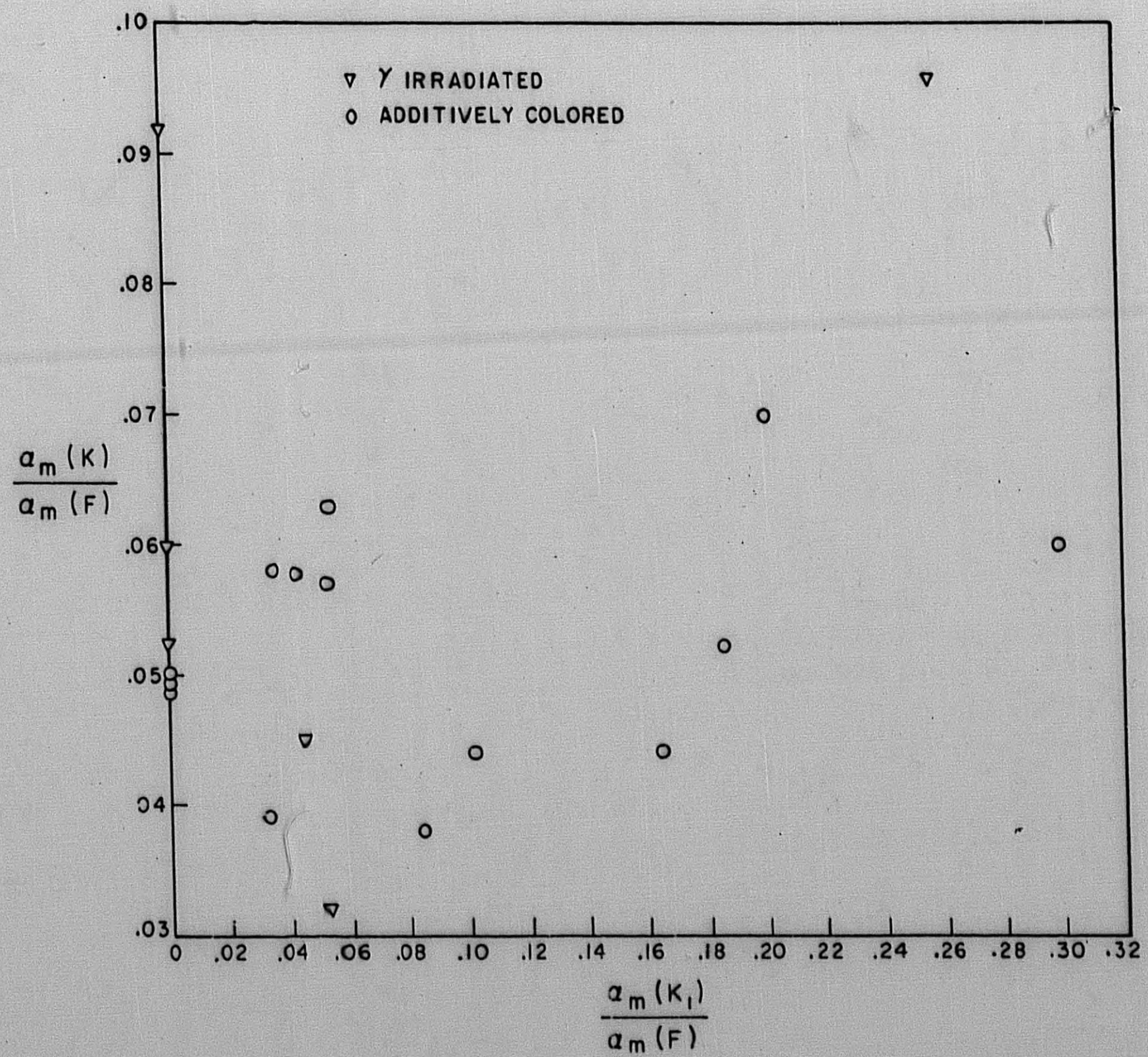


Figure 3. The K to F ratio versus the K_1 to F ratio in γ -irradiated and additively colored RbCl.

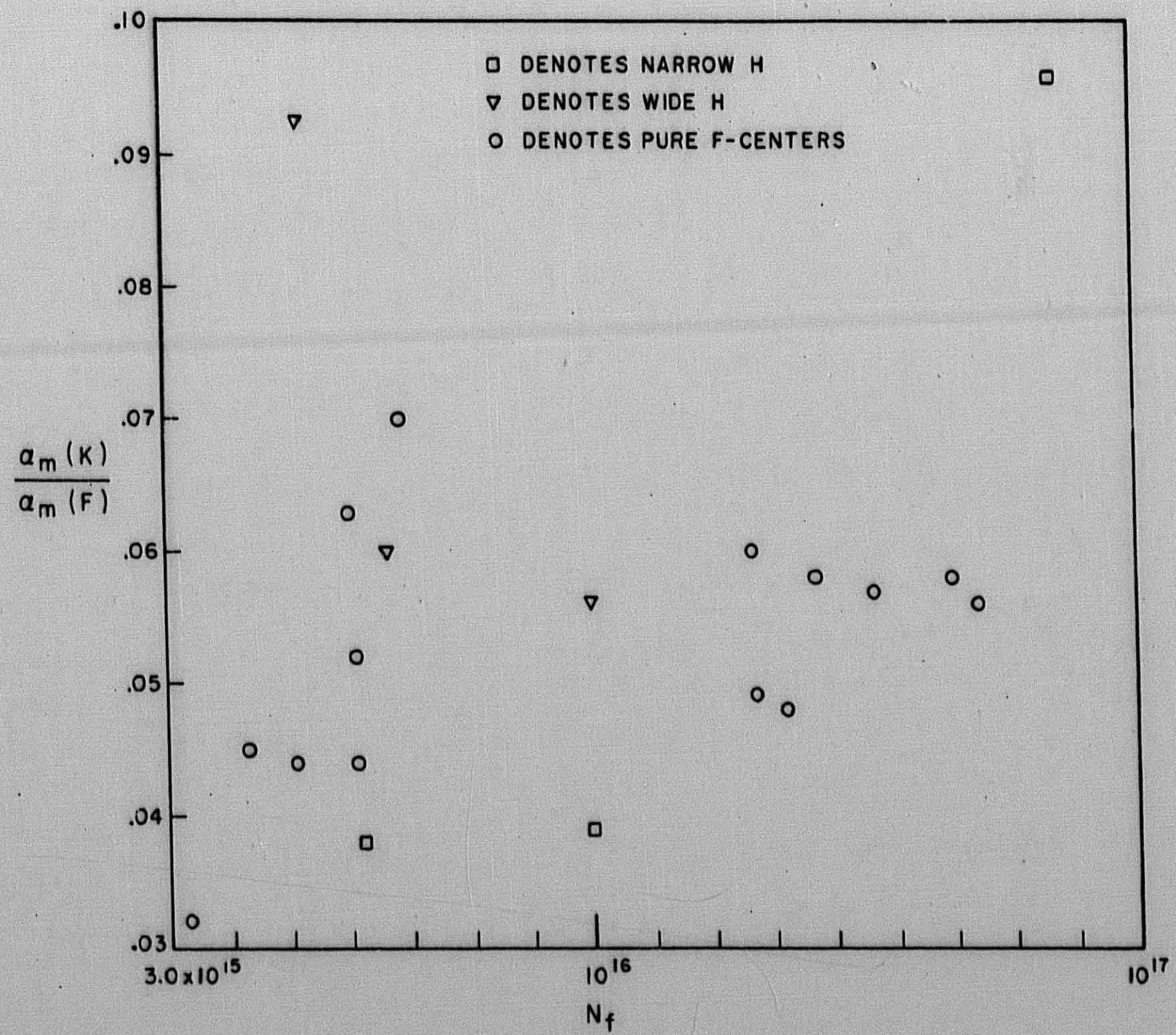


Figure 4. The K to F ratio versus the F-center concentration N_f in γ -irradiated and additively colored RbCl.



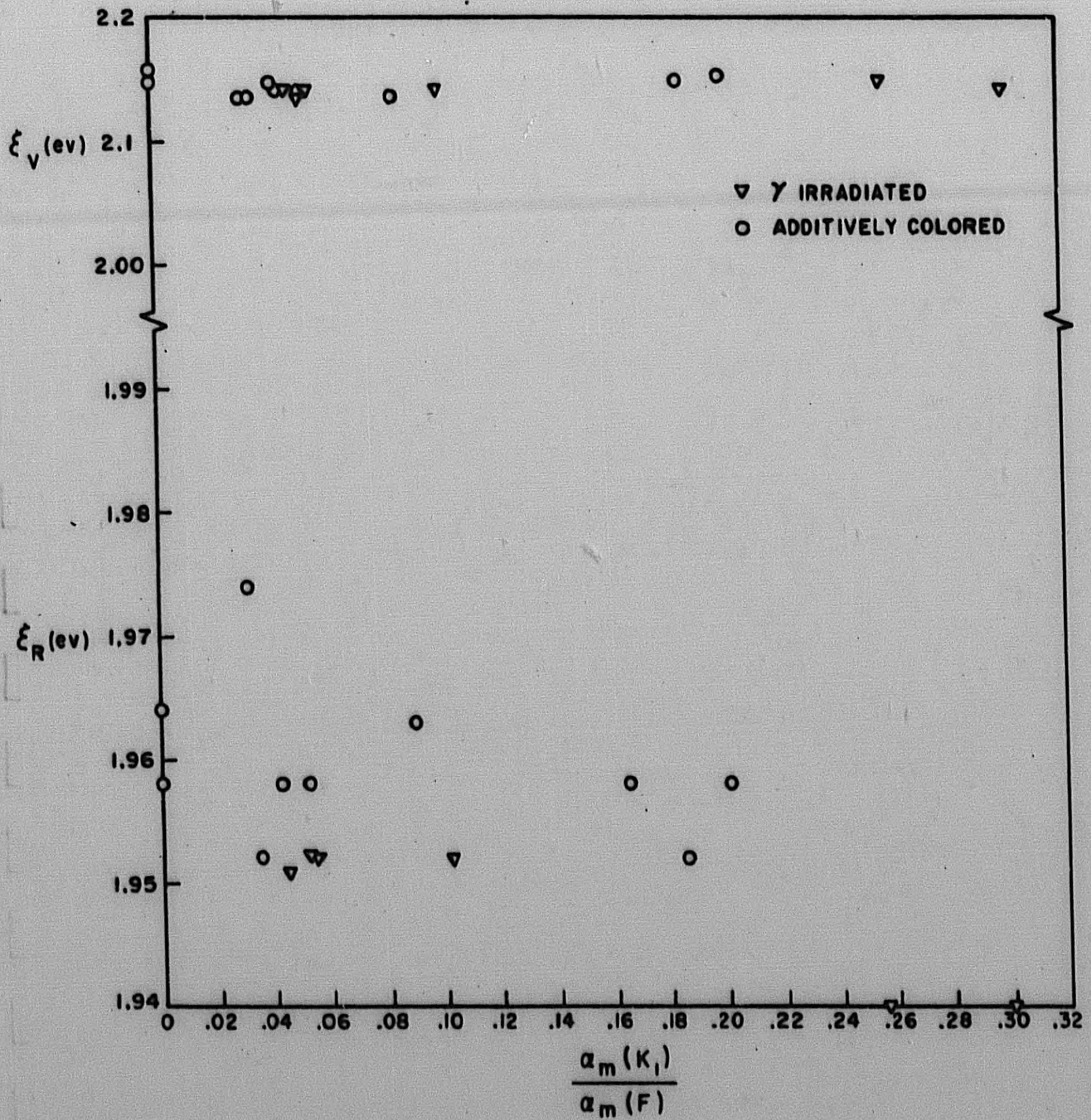


Figure 5. The K_1 to F ratio versus the F-band parameters ϵ_v and ϵ_r , in γ -irradiated and additively colored RbCl.

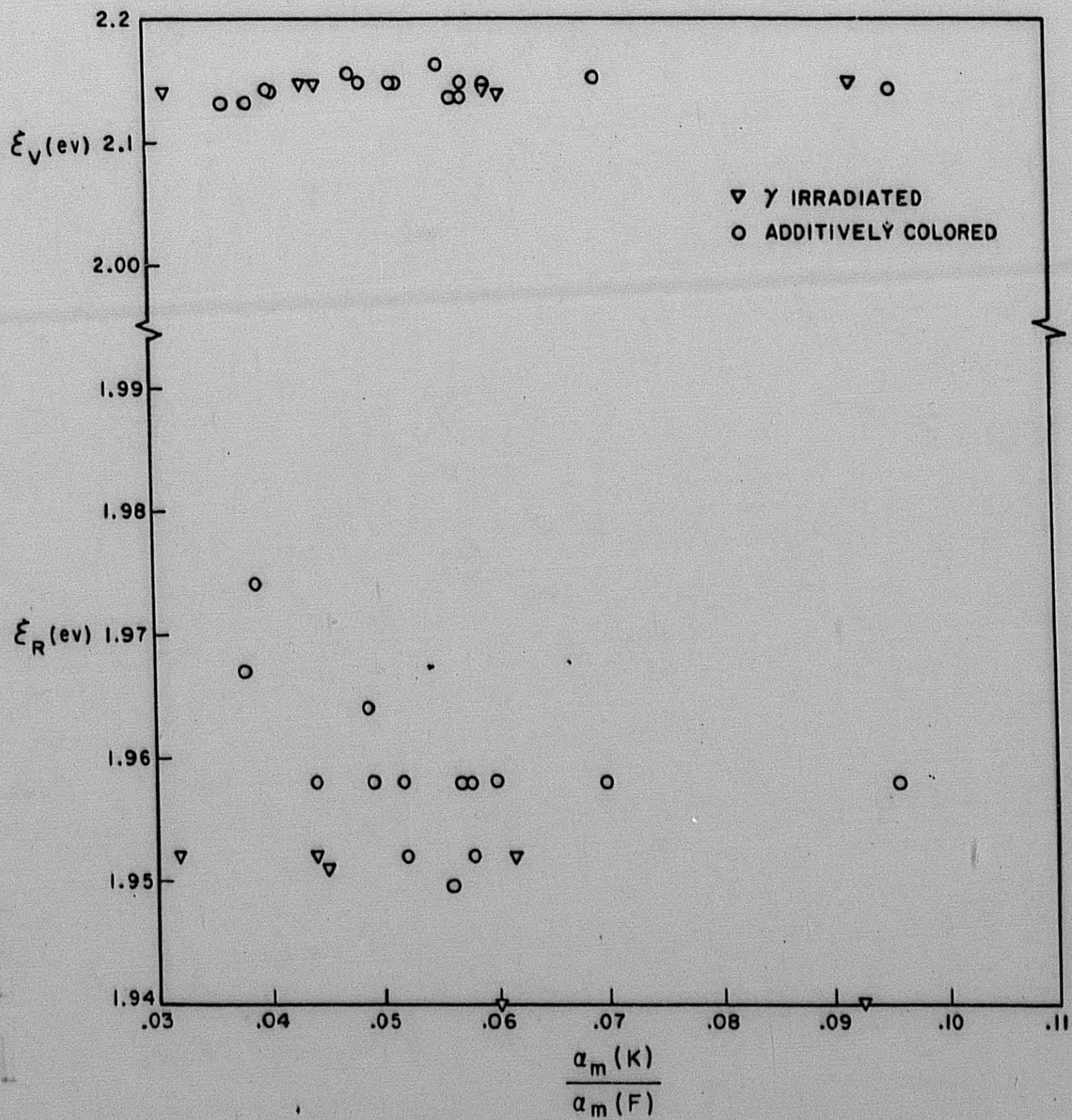


Figure 6. The K to F ratio versus the F-band parameters, ϵ_V and ϵ_R in γ -irradiated and additively colored RbCl.

ϵ_r . Here the red side seems to be independent of the K-band. This is also true for ϵ_v . This is most important since one would expect a large deviation in the K-band to cause a corresponding deviation in the violet side of the F-band.

Figure 7 is a graph of the K to F ratio versus the half-width H. The value for H which depicts a pure F-center is $(0.190 \pm .03) \text{ev}^{11}$ at 78°K . Here we see again a large deviation in the K to F ratio even for the case of pure F-centers.

From the data presented, we may draw the following conclusions:

- (1) The K to F ratio is not constant which implies that the K-band is not a transition of the F electron to higher excited states.
- (2) The K to F ratio deviation does not depend upon the concentration of M-centers which were present.
- (3) The K to F ratio does not seem to be influenced by the presence of the K_1 -band.
- (4) The K_1 -band does not influence the values of the parameters which characterize the F-band.
- (5) The K to F ratio is independent of the F-center concentration (if the densities involved are not too great).
- (6) The deviation in the K to F ratio does not influence the parameters ϵ_v , ϵ_r and H.

We have been able to obtain some purified RbCl from Anderson Laboratories in Urbana. We hope this will eliminate the large variations in ϵ_r , and H. We feel certain that this additional data will shed light on the K to F ratio and perhaps lead to a better understanding of the F-center.

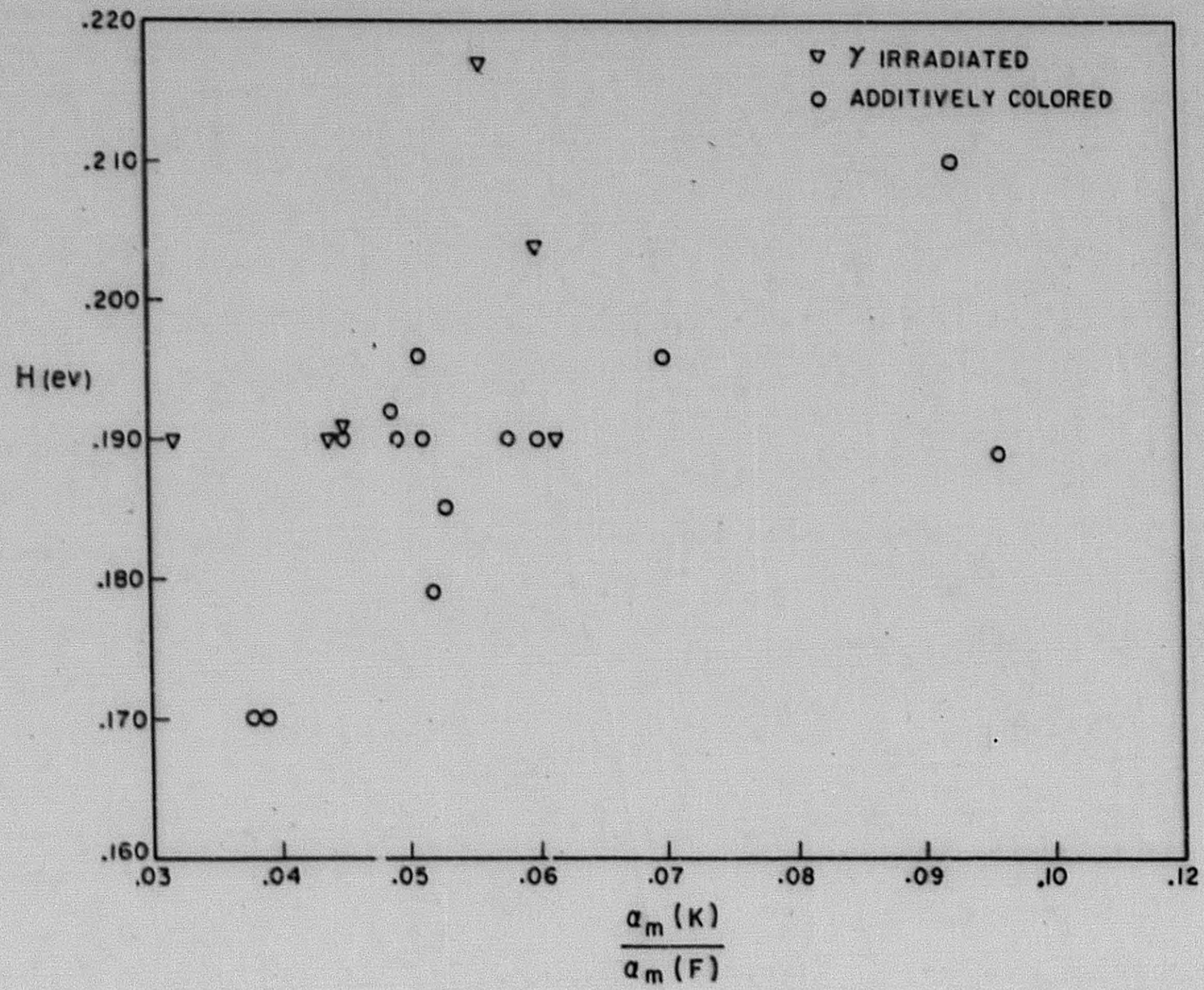


Figure 7. The K to F ratio versus the half width H in γ -irradiated and additively colored RbCl.

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II. PROPOSED LUMINESCENCE EXPERIMENTS AND EQUIPMENT

It is proposed to measure the following four properties of the F-center luminescence starting with RbCl:

- I. Light intensity influence on total luminescence.
- II. The temperature dependence of the total luminescence.
- III. The possible influence of F-center concentration on the total luminescence.
- IV. The spectral distribution of the emitted light, at various temperatures. (If possible, wavelength of the exciting light would be varied as well, in order to detect any other luminescent bands whose optical absorptions could be masked by the F-band).

The Experimental Set-Up

The set-up for all of the first three (I-III) experiments will be essentially the same (Fig. 8). The crystal investigated (F) will be mounted in an optical cryostat and illuminated by a beam of light at an angle of incidence of 45° . The light beam will originate in a concentrated arc source (B) and pass through an optical collimating system and light filters (C, B). As the wavelengths of the D emission lines of sodium are in the right spectral region for F-band stimulation of RbCl, it would be advisable to use a sodium arc, if available. Other possible light-sources would be a xenon arc or a concentrated arc of the argon-zirconium type. As these last mentioned light sources have a rather continuous spectral distribution, filters or a monochromator would have to be used in order to decide the spectral distribution of the light falling on the crystal. Before reaching

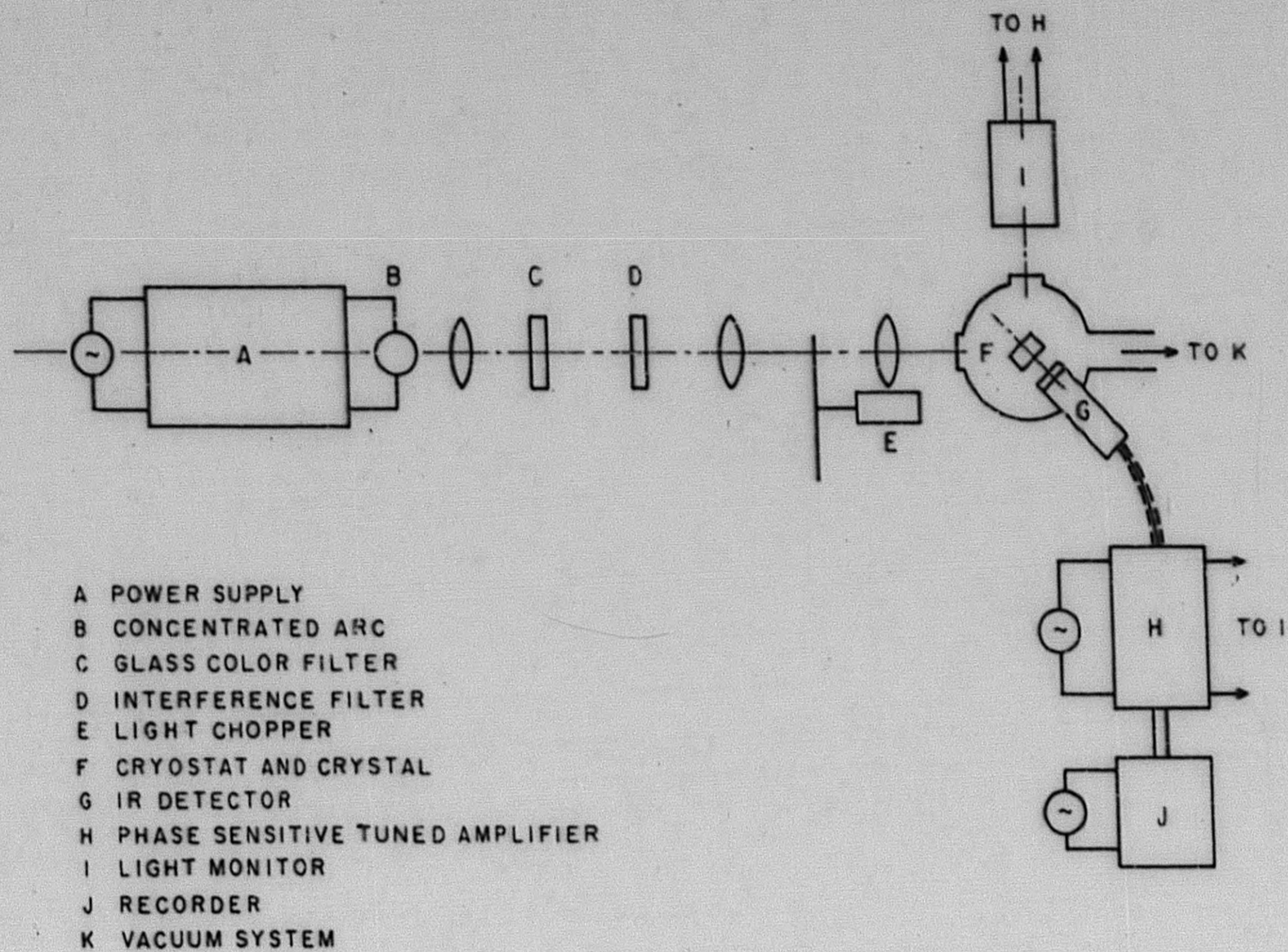


Figure 8. Apparatus for study of total luminescence.

the crystal (F), the light beam would pass through a revolving light-chopper (E), which would modulate the light beam at a reasonable audio frequency. The beam reflected from the surface of the crystal will be detected by a detector (I). This signal will be used for two purposes; providing a reference signal of the right phase and frequency, and for intensity control of the primary light beam. This detector could either be a solid state device or a vacuum device. As vacuum devices (such as photomultipliers) are generally more linear in their light intensity response, they seem to be preferable in this case.

The luminescent radiation itself should be measured in a way which excludes serious interference by the primary light beam, i. e., at such an angle in respect to this beam, that no direct primary light can reach the I. R. radiation detector (G). Another filter excluding the primary radiation will certainly be needed in front of this detector. This unit will most probably be made up from a PbS photoconductive cell mounted on a cooled base and provided with a suitable power source and preamplifier. The output of this preamplifier will be fed into a tuned, phase-sensitive amplifier (H). This amplifier would obtain its reference voltage from the monitor (I). The I. R. radiation detector system will have to be calibrated carefully for its wavelength and intensity response. The output of the amplifier (H) will be fed into a recorder (J).

More experimental difficulties are to be expected in experiment IV (Fig. 9). As before, the crystal would be illuminated through an optical system containing optical filters or a monochromator (C). The light path will be similar, and again the primary beam will be monitored (H). The emitted luminescent radiation has to be collected by an optical system and

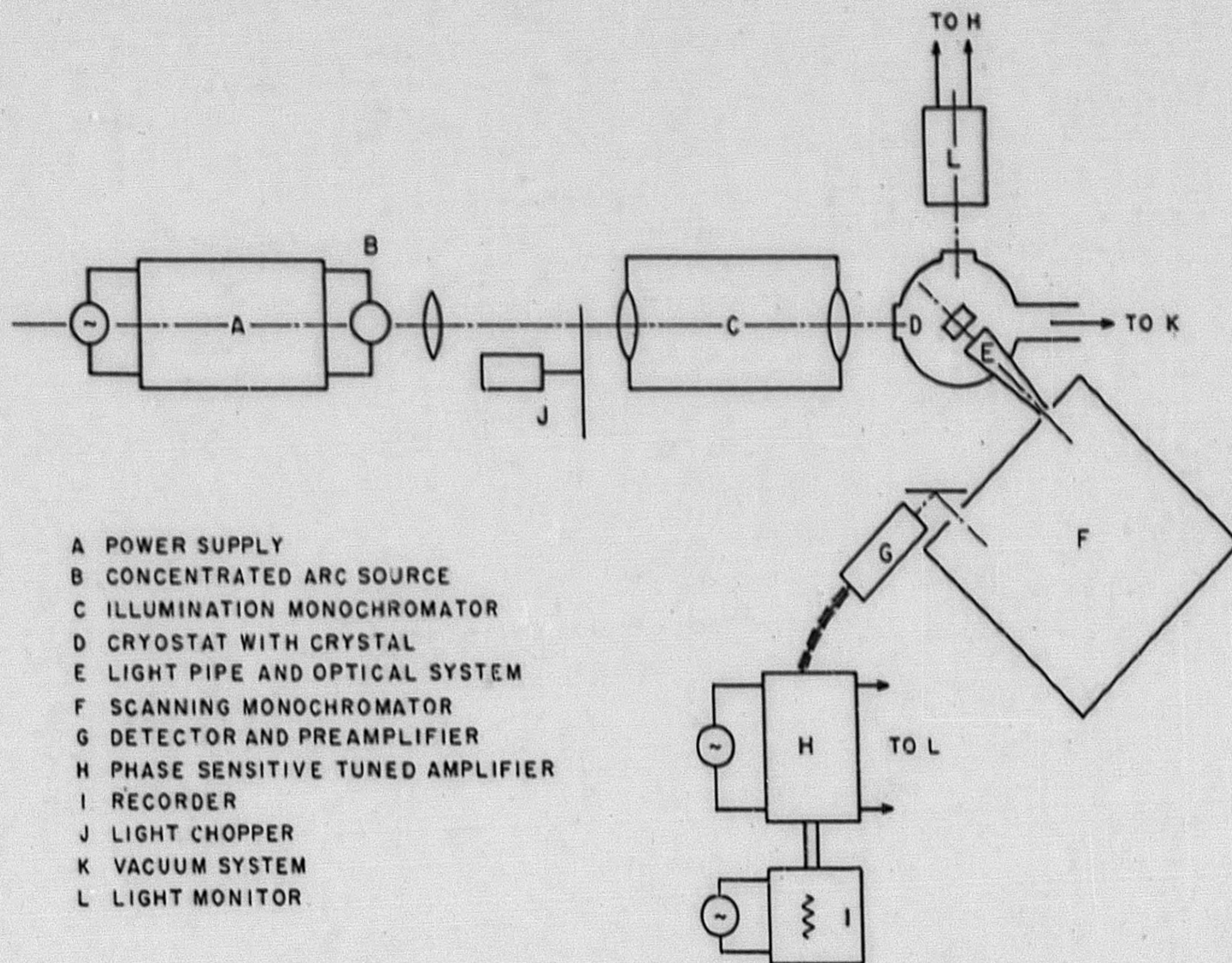


Figure 9. Apparatus for study of the band shape of the luminescence.

injected into the entrance slit of an I. R. scanning monochromator (F). The light output at the exit slit of this monochromator would again be measured in a way similar to that described previously. As the luminescent band is quite broad* (9000 Å to 15,000 Å and extending up to 17,000 Å when M centers are present) the monochromator range should extend up to about 20,000 Å. Because of linearity of scale and higher aperture, a grating monochromator has been chosen for this purpose.

The design and building of the equipment is the responsibility of Dr. Brada, and the equipment purchased for this purpose will be obtained without cost to this contract.

* Botden, Doorn, Haven, Philips Res. Rep. 9, 469 (1954).

III THE LIFETIME OF THE F-CENTER

The lifetime of the F-center in KCl has been measured by Swank and Brown; and has been calculated by Mott and Gurney, by Fowler and Dexter, as well as by the author. The values for KCl are as shown in the table.

TABLE

Measured - Swank and Brown ¹	577×10^{-9} sec.
Calculated - Mott and Gurney ²	69×10^{-9} sec.
Calculated - Fowler and Dexter ³	93×10^{-9} sec.
Calculated - Markham ⁴	6.2×10^{-9} sec.

The need to correct the usual Einstein A coefficient for use in the theory of defects in solids predates this work. Pekar⁵ suggested a correction in 1952, but the exact formal correction first appears in a paper by Lax⁶, also in 1952. Lax's paper was subsequently reviewed by Dexter⁷.

The table suggests several problems. We shall ignore the value of Mott and Gurney since their equation is only a rough order of magnitude. Fowler and Dexter⁸ (referred to by the letters FD) and Markham's value (referred to by JM) are presumably reliable values and the order-of-magnitude of the difference between them remains completely unexplained. The second problem of greater interest is why there is such a large difference between the theoretical and the experimental values. JM's value is off by a factor of 93. However, FD's value is off by only 6, which in view of the many necessary approximations does not seem as serious to the theorist as one might first expect. Our first objective is to examine the factor of 15 between the theoretical values which occurs due to a series of assumptions which always tend to make the calculation of FD larger than JM's.

Many of these assumptions deserve further study and are subject to question. One difference is caused by an arithmetic error which halves the value of FD.

FD used the following equation to calculate the lifetime of the excited state

$$\tau(\text{FD}) = \frac{9\hbar^2 c^3 m E_{uk} [2J(P_k) + 1 + 2J(P_{3/2}) + 1]}{(n^2 + 2)^2 n f_G(\rho_u) 2e^2 E_{\rho_u}^3 [2J(S_{1/2}) + 1]} \quad (1)$$

Eq. (1) was obtained from FD's Eq. (22) using the following notation:

- (1) $m \rightarrow \ell$ (lower).
- (2) $k \rightarrow u$ (upper).
- (3) n is the index of refraction.

The following assumptions were made by FD:

- (1) Matrix elements of \underline{r} for a transition from ℓ to u equals the matrix elements for a transition from u to ℓ ;
- (2) The emission is due to transitions from a $P_{1/2}$ to the lower $^2S_{1/2}$ state as well as from $^2P_{3/2}$ to the $^2S_{1/2}$;
- (3) $E_{u\ell}$, the energy of an emitted photon, equals 1.26 e.v. for the F-center in KCl not 1 e.v. as quoted by FD. This introduces an error of $(1.28)^3$ in the denominator of Eq. (1) and one must divide their result by 2.1. $J(P_{1/2})$ is the J th quantum number of the $P_{1/2}$ state and $h, c, m,$ and e have their usual values. Thus $\tau(\text{FD})$ really is 4.6×10^{-9} sec. and the ratio $\tau(\text{FD})/\tau(\text{JM}) = 7.5$.

f_G is the oscillator strength when a Gaussian or a Pekarian band shape is assumed. As long as one uses the oscillator strength in conjunction with the maximum absorption and the width at half height, one may use any experimental oscillator strength since the value of f is compensated by

the value of the Smakula constant (a_s) assumed.⁹ This is not the case when one "integrates" over the absorption and the emission bands. The oscillator strength pertaining to the true absorption curve must be used i. e. the Pekarian or the Gaussian.

The reader should note that FD assumes that the basic quantity which remains invariant during the adjustment of the lattice is the matrix element of x . Further, they assume that the F-center has complete spherical symmetry so that l , s and j are good quantum numbers. We shall shortly show they also assumed that there is no spin-orbit coupling in the excited state.

As pointed out previously¹⁰ we do not know whether one should assume that the matrix element of x or of p should be invariant for the process $l \rightarrow u$ and $u \rightarrow l$. A further possibility exists that neither is invariant, but that f , the oscillator strength is. The reader is reminded that the sum rule is in terms of the oscillator strengths not the matrix elements. If an imperfection has only two bound levels and, direct transitions to the conduction bands were forbidden, then f will not be affected by changes in the energy interval between the l and u levels due to the readjustment of the levels. This might be the case for the F-center if, indeed, the K and the L-bands are not connected to this imperfection.

The equation for the lifetime used by JM was of the form

$$\tau_{ul}(\text{JM}) = \frac{9\hbar^2 c^3 m}{n(n^2+2)^2 f_L(lu) 2e^2 E_{lu}^2} = \frac{9\hbar^2 c^3 m}{n(n^2+2)^2 f_G(lu) 2e^2} \frac{a_s(G)}{a_s(L) E_{lu}^2} \quad (2)$$

Equation (2) assumes that there is one lower and one upper state and further, that the degeneracy is only due to the spin and that f is invariant. The ratio of the two quantities from Eqs. (1) and (2) is

$$\tau_{ul}(FD)/\tau_{ul}(JM) = 3 \frac{a_s(L)}{a_s(G)} \frac{E_{ul}}{E_{LH}} \quad (3)$$

since $[2J(P_{1/2})+1 + 2J(P_{3/2})+1]/[2J(S_H)+1] = 3$

Equation (3) resolves the dilemma between the results of Fowler and Dexter and that of the author, since $\int_{ul}(FD)/\int_{ul}(JM) \approx 8$, but it does not get to the heart of the problem which is to explain the results of Swank and Brown. The most conservative estimate i. e. the longest time is a factor of 14 times too short and the agreement is completely unsatisfactory. If $P_{1/2}$ and $P_{3/2}$ levels are separated, due to spin-orbit coupling, then the factor increases since we need only consider the lower state. We have good experimental evidence that the first excited state is very narrow (no spin-orbit splitting) and that it is not a series of bands. The difference, hence, must be at least of the order of 20. This suggests that both calculations do not attack the fundamental reason as to why the theory does not explain the results of Swank and Brown.

In the paper of Fowler and Dexter, they attempt to develop a theory of transitions which is in variance with the development of a theory by the author to treat the same problems. Detailed application of either theory has not been made. In view of the failure of the calculations, such application seems to be in order at the present time.

Fowler and Dexter point out that the simplest theory of the Einstein A and B coefficients do not apply to complex solids. This is certainly true and almost expected, but the author cannot agree with FD that the whole concept of the coefficients should be abandoned. Certainly this is an unwarranted step at our present limited degree of knowledge. In principle, in very many ways, imperfections in solids behave very much like mole-

cules. We therefore, plan to study the properties of the A and B coefficients in full detail, going back to the original treatment and combine it with the Born-Oppenheimer technique of writing wave functions. A large change in $\langle | \underline{g} | \rangle$ will be reflected in the form of the absorption band and emission bands.

References for Part III

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- 3) W. B. Fowler and D. L. Dexter, *Phys. Rev.* 128, 2154 (1962).
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- 8) FD assumed that a numerical error exists in JM's value which is not the case.
- 9) FD quotes an alternate equation but show that this equation is equivalent to their Eq. (22), our Eq. (1). One must be careful to use the oscillator strength which corresponds to the actual absorption shape. In general this is not an important problem but in this particular case, it is. For a detailed discussion, see J. J. Markham, *Rev. Modern Phys.* 31, 967 (1959).
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